EXPERIMENTAL STUDY OF THE DENSITY AND DERIVED PARTIAL MOLAR VOLUMES OF TERNARY WATER+1-PROPANOL+POTASSIUM NITRATE MIXTURES AT TEMPERATURES FROM (303 TO 448) K AND PRESSURES UP TO 35 MPA

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Densities of ternary water+1-propanol+KNO3 mixtures have been measured over the temperature range from (303 to 448) K and at pressures up to 35 MPa using the constant-volume piezometer immersed in a precision liquid thermostat. The effect of salt and alcohol concentrations on the ternary mixture density and partial molar volumes were studied. The derived volumetric property such as partial molar volumes of salt (KNO3, ) and alcohol (1-propanol, ) were calculated using the measured values of the ternary mixture densities. The volumetric behavior of the ternary mixture was interpreted in term of changes in the water structure caused by the added alcohol (1-propanol) and salt (KNO3). It was shown that changes in the volumetric behavior of the complex solutions are results of the structural changes in water structure caused by solutes (alcohol and salt). In several previous publications we have studied the density and derived volumetric properties of binary water+1-propanol [1], water+ethanol, and ternary water+ethanol+LiNO3 mixtures [2]. The same apparatus we used previously to measure of the volumetric properties (*PVTx*) of binary aqueous 1-propanol [1] and KNO3 [3] mixtures at high temperatures from (298 to 573) K and high pressures (up to 40 MPa). the primary objective of this work was to provide new reliable experimental volumetric (density) and derived (partial molar volumes) properties for ternary water+1-propanol+KNO3 mixtures at high temperatures (up to 448 K) and high pressures (up to 40 MPa). This work is a part of continuing program on the study of thermodynamic and transport properties of binary and ternary aqueous electrolyte solutions at high temperatures and high pressures. The details of the uncertainty analysis for the density and derived volumetric properties (,,) for the method is given in our recent publication [1,2].

New density data for ternary water+1-propanol+KNO3 mixtures have been measured over the temperature range from (303 to 448) K and at pressures up to 35 MPa using a constant-volume piezometer technique for six concentrations, namely: (1) KNO3(0.0077 mole %)–С3Н7ОН (1.55 mole %); (2) KNO3(0.0077 mole %) – С3Н7ОН (5.02 mole %); (3) KNO3 (0.0077 mole %)–С3Н7ОН (6.97 mole %); (4) KNO3 (0.0126 mole %) – С3Н7ОН (5.02 mole %); (5) KNO3 (0.0308 mole %)–С3Н7ОН (5.02 mole %); and (6) KNO3 (0.0077 mole %)–С3Н7ОН (9.08 mole %). The partial molar volumes of salt (KNO3) ,, and alcohol (1-propanol) , ,were calculated using the measured density data for the ternary water+1-propanol+ KNO3 mixture as a function of temperature, pressure, and concentrations. The partial molar volume maximum was found at temperatures around 323 K at low (dilute concentrations of salt) and considerable shift to high temperatures (up to 373 K) at high concentrations of 0.0308 mole %. The pressure slightly changes the location of the temperature maximum of . The concentration dependences of the derived partial molar volumes of salt were extrapolated to zero concentration (=0) to yield the partial molar volumes at infinite salt dilution (). The temperature, pressure, and concentration dependence of density and derived partial molar volumes of the ternary mixture were studied. As one can see from Fig. 1, all measured isobar-isopleths for the mixture in *ρ*-*T* projection shows the behavior close to the quadratic functions of temperature, just like for pure water (solid line). Therefore, the temperature behavior of density of the ternary water+1-propanol+KNO3 mixture basically governs by water’s properties. The density of binary water+1-propanol mixture is lower than pure water and ternary mixture densities (see Fig. 1). It is apparent that when alcohol (1-propanol) is added to water, density of the mixture decreases because the density of alcohol is less than that of water. Instead, by adding salt to an aqueous solution, the density increases because salt density is greater than that of water. Organic (alcohol) and inorganic (salt) solutes have the opposite effect on the density behavior mixture and water structure changes (structure forming and breaking effects) in the mixture. These two opposite competition effects are determined the solution density and other thermodynamic properties behavior. It is apparent that the density of the ternary mixture depends on the relation between the salt and alcohol concentrations. As one can see from Fig. 1, the addition of salt to binary water+1-propanol (=5.02 mole %) mixture increases the density of the ternary solution and at salt concentrations above =0.0077 mole % becomes higher than the pure water density. The pressure dependence of the present density measurements for ternary water+1-propanol+KNO3 mixtures along the two selected experimental isotherms (303.15 and 448.15 K) and various concentrations of alcohol (1-propanol) at fixed concentration of salt (=0.0077 mole %) is shown in Fig. 2 together with pure water values. As this figure demonstrates, all experimental density isotherms for various concentrations of salt (KNO3) and alcohol (1-propanol) are lie on straight lines with the same slopes (linear function of pressure). As we can note from Fig. 2, pure water density higher than the ternary solution with salt concentration of =0.0077 mole %at alcohol concentrations below 6.97 mole % at temperature of 303.15 K, while for the isotherm of 448.15 K the density of pure water higher than for solution at alcohol concentrations below 5.02 mole %. This figure demonstrates the effect of temperature on the character of water structure changes in the solution with given concentrations of alcohol and salt (simultaneous effect of temperature and concentrations of solutes at fixed pressure).

The partial molar volumes of the salt at infinite-dilution  are small affected by temperature in the low temperature range (below 350 K) and rapid decreasing at high temperatures (above 350 K). The pressure dependence of is very small at low temperatures 350 K, while at high temperatures the slope of the -*P* isotherms sharply changes. In the presence of the alcohol in the binary water+KNO3 solution at the same *T* and *P* conditions the partial molar volume of salt (KNO3) is increasing in compare with the values alcohol –free binary water+KNO3 solutions. For example, the addition of 5.02 mole % alcohol (1-propanol) into binary mixture of water+KNO3 the partial molar volume of the salt is slightly (by 7.5 %) increasing. The structure related properties such as partial molar expansibilities of alcohol (1-propanol)  and salt (KNO3)  and their curvatures, , which are sensitive measure of the effect of solutes on the structure of water, were calculated using the experimental density data. The partial molar expansibilities of alcohol, >0, and salt, <0, have the opposite signs and opposite temperature dependences. The same signs and temperature dependences were observed for second temperature derivatives (curvature), >0 (structure maker solute) and <0 (structure breaking solute), of partial molar volumes of alcohol and salt, respectively. The molar expansibilities of pure water,, and pure 1-propanol, , and their curvatures,  and 1-propanol,, at the same *T* and *P* conditions are positive.



**Fig. 1.** Measured densities of pure water, binary water+1-propanol, and ternary water+1-propanol+KNO3 mixtures as a function of temperature for two selected isobars and various concentrations of electrolyte (KNO3) at fixed concentration of alcohol (1-propanol, **=5.02 mole %). ○, **=0.0 (binary water+1-propanol mixture **=5.02 mole % [5]); ●, ** = 0.0077 mole %; △, ** = 0.0126 mole %; ▲, ** = 0.0308 mole %; Solid lines are pure water values (IAPWS). Dashed lines are interpolated values.



**Fig. 2.** Measured densities of ternary water+1-propanol+KNO3 mixtures as a function of pressure for two selected isotherms (303.15 K, left and 448.15 K, right) and fixed concentration of salt (**=0.0077 mole %) for various concentration of alcohol (1-propanol). ○, **=9.08 mole %; △, **=6.97 mole %;●, **=5.02 mole %;▲, **=1.55 mole %; □, **=0 mole % (binary water+KNO3 mixture). Solid lines are pure water values (IAPWS). Dashed lines are interpolated values.

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